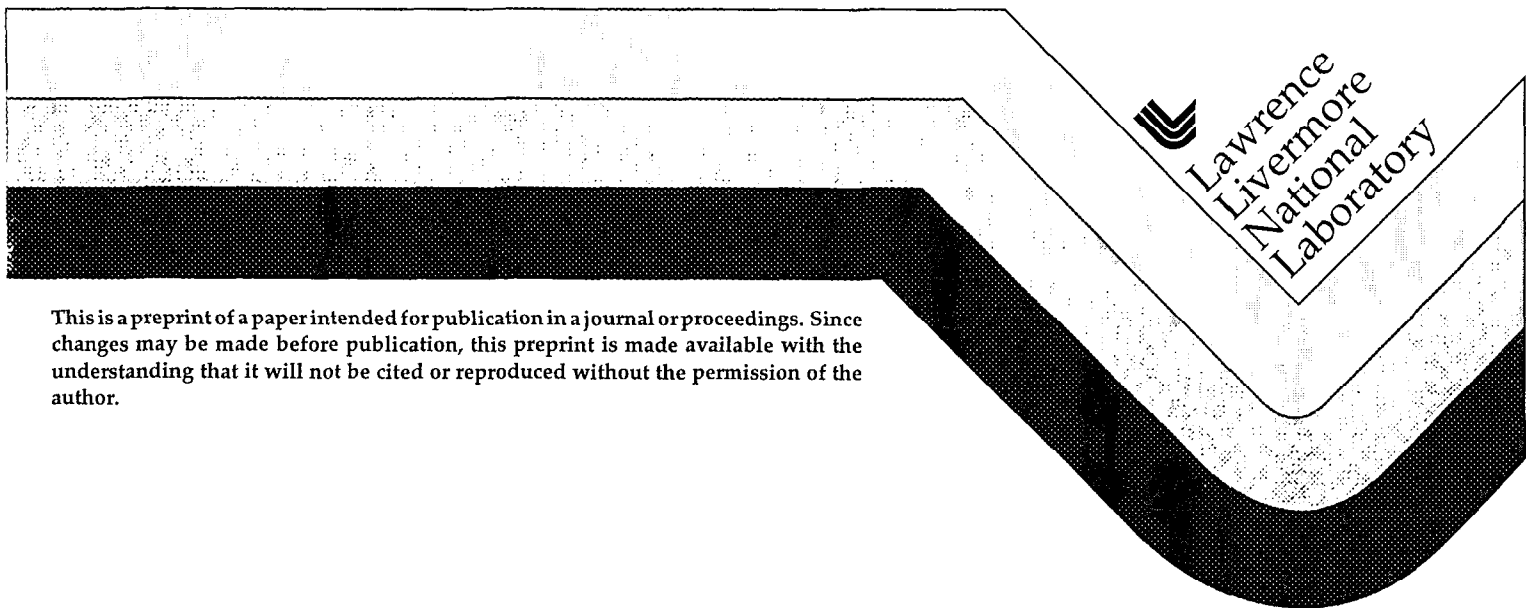# Picosecond Nonradiative Processes in Neodymium-doped Crystals and Glasses: Mechanism for the Energy Gap Law

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# Picosecond Nonradiative Processes in Neodymium-doped Crystals and Glasses: Mechanism for the Energy Gap Law*

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## Abstract

We present measurements of the $^4G_{7/2}$ emission lifetime for 26 Nd-doped materials. A model of nonradiative decay based on dipole-dipole energy transfer is developed and found to be supported by our data.

## Introduction

It has been extensively verified in the past that the nonradiative decay rate between rare earth energy levels is predominantly determined by the energy gap and the particular host medium. The *energy gap law* is embodied in the simple expression for the nonradiative rate:

$$W_{nr} = (1/\tau_0)\exp(-a \cdot p), \qquad (1)$$

where $\tau_0$ and $\beta$ are constants characteristic of the host medium, and p ($=\Delta E / h\upsilon_{max}$) is the number of phonons needed to bridge the gap. The expression $h\upsilon_{max}$ is related to the highest phonon frequency of the host medium and $\Delta E$ is the energy gap between the populated rare earth state and the next energetically lower level. The constant, *a*, is related to the details of the electron-phonon coupling. In nearly all cases reported in the literature, eqn. (1) is regarded as adequately describing the measured decay rates over several orders of magnitude [1-3].

In the present paper we report the nonradiative decay rates of the $^4G_{7/2}$ state of $Nd^{3+}$ in 26 different crystals and glasses, with the goal of providing a data base relevant to the relaxation rate of the $^4I_{11/2}$ state which has a similar energy gap as the $^4G_{7/2}$ state [4]. The $^4I_{11/2}$ state of $Nd^{3+}$ is a particularly important one from a practical point of view, since it can potentially "bottleneck" during lasing and give rise to transient absorption at the laser wavelength (constituting loss).

Much of the motivation for establishing this correlation is that emission lifetimes are much simpler to measure and can be widely applied to numerous Nd-doped crystals and glasses, while the pump-probe technique used to directly assess the $^4I_{11/2}$ decay time is complex to set up and execute.

The relevant energy levels are depicted in Fig. 1, where the $\tau_{5/2}$, $\tau_{7/2}$, and $\tau_{11/2}$ lifetimes are identified on the diagram along with the 532 nm pump wavelength and the ~600 nm detection wavelength One of the details that must be handled in the numerical analysis of the data is the effect of the overlapping ~600 nm emission arising from the $^4G_{5/2}$, $^2G_{7/2}$ states on the measured results (i.e. $\tau_{5/2}$), as depicted in Fig. 1. The numerical analysis and resulting fits to the data will be discussed.
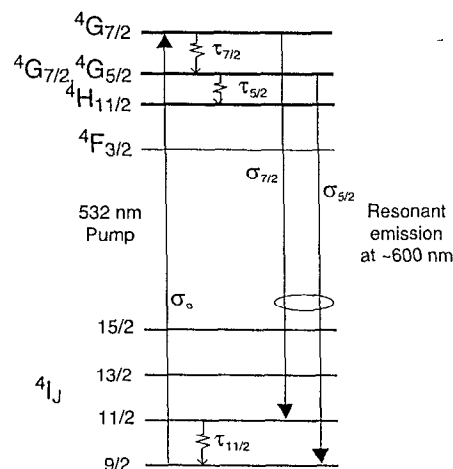


Fig.1 Energy levels and transitions for $Nd^{3+}$

## Experimental

The picosecond emission lifetimes [4] were measured using the time-correlated single photon counting system together with a Coherent mode-locked laser producing ~90 psec pulses at 76 MHz and then doubled to 532 nm. The sample emission was detected at ~600 nm with a monochromator followed by a multichannel plate photomultiplier (MCP-PMT). The (deconvoluted) temporal resolution of the data is about 50 psec. For the case of the fluoride samples, the lifetimes of ~10 nsec were too long to be measured with the time-correlated photon-counting apparatus. To handle these longer lifetimes, we employed a conventional set-up consisting of a Q-switched Nd:YAG laser (12 nsec pulsewidth), along with a monochromator, oscilloscope, and MCP-PMT

## Results

The results of the emission lifetime experiments are contained in Table 1. Based on an analysis of the best fit to the data, the uncertainty in the value of the $\tau_{7/2}$ lifetimes is $\Delta\tau_{7/2}$ (<1 ns) = ± 50 ps for data with lifetimes less than 1 ns and $\Delta\tau_{7/2}$ (>1 ns) = ± 200 ps for data with lifetimes greater than 1 ns.

Many of the trends that can be gleaned from the data in Table 1 are expected. For the case of the fluorides, the $\tau_{7/2}$ values are the longest, being 4,000 - 41,000 psec. This is anticipated, since their phonon

frequencies are the lowest among the hosts listed, being $<600$ cm$^{-1}$. Whereas the phosphate and silicate glasses are in the range of 150 to 250 psec owing to the rather high vibrational frequencies of the $SiO_4$ and $PO_4$ anions. It is noteworthy that comparisons of previous $\tau_{7/2}$ measurements in the literature are satisfactory, including [5]: 1400 versus 1090 psec for $YAlO_3$; 370 versus 200 psec for $Y_3Al_5O_{12}$; and 8400 psec versus 9100 psec for $LiYF_4$; 56,400 psec versus 41,000 psec for $LaF_3$

**Table 1.** Emission lifetimes of the $^4G_{7/2}$ excited state $(\tau_{7/2})$

| Name | Formula | $\tau_{7/2}$, psec |
|---|---|---|
| **Phosphate glasses** | $P_2O_5+Al_2O_3+$ modifiers | |
| LG-750 | | 228 |
| APG-1 | | 215 |
| APG-x | | 210 |
| APG-2 | | 150 |
| LG-812 | $P_2O_5+$fluorides+ modifiers | ~1400 |
| **Silicate glasses** | $SiO_2+Al_2O_3+$ modifiers | |
| LG-660 | | 215 |
| LG-650 | | 210 |
| Sol-gel | $SiO_2$ | 245 |
| **Vanadate** | | |
| YVO$_4$ | $YVO_4$ | 190 |
| **Tungstate** | | |
| CaWO$_4$ | $CaWO_4$ | 510 |
| **Oxide** | | |
| YALO | $YAlO_3$ | 1090 |
| GSGG | $Gd_3Sc_2Ga_3O_{12}$ | 715 |
| YAG | $Y_3Al_5O_{12}$ | 200 |
| GGG | $Gd_3Ga_5O_{12}$ | 530 |
| LLGG | $La_3Lu_2Ga_3O_{12}$ | 1200 |
| **Apatites** | | |
| C-FAP | $Ca_5(PO_4)_3F$ | 70 |
| S-FAP | $Sr_5(PO_4)_3F$ | 175 |
| C-VAP | $Ca_5(VO_4)_3F$ | 200 |
| S-VAP | $Sr_5(VO_4)_3F$ | 330 |
| ------ | $Sr_5(VO_4)_3Cl$ | 380 |
| **Fluorides** | | |
| ZBLAN | $ZrF_4$-$BaF_2$-$AlF_3$-$LaF_3$-NaF | 18,000 |
| YLF | $LiYF_4$ | 9100 |
| Na$_3$Sc$_2$Li$_3$F$_{12}$ | $Na_3Sc_2Li_3F_{12}$ | 4000 |
| KY$_3$F$_{10}$ | $KY_3F_{10}$ | 9000 |
| YF$_3$ | $YF_3$ | 22,000 |
| LaF$_3$ | $LaF_3$ | 41,000 |

## Analysis and Discussion

As mentioned earlier, measurements of the $^4G_{7/2}$ population decay time have long been suspected to be similar in magnitude to that of the $^4I_{11/2}$ level of $Nd^{3+}$. Using the $^4I_{11/2}$ lifetimes from a direct measurement in [7] we find that the $^4I_{11/2}$ and $^4G_{7/2}$ lifetimes are

correlated with each other to within about a factor of two, across a variety of different host media. This concurrence is reasonable, since some differences in the energy gap and perhaps the electron-phonon coupling may be expected, in addition to the experimental and analytical uncertainties. Furthermore, due to the small difference in the size of the energy gap for a given host medium, this data offers some experimental validation that the specific characteristics of the electronic states (symmetry, crystal field interactions, spin, etc.) do not strongly influence the nonradiative decay rate.
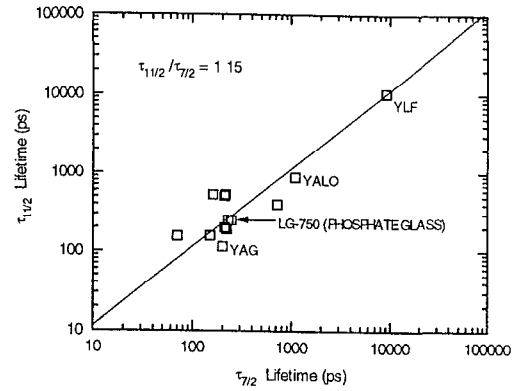


Fig. 2 Comparison of the $^4I_{11/2}$ nonradiative relaxation time from [4] and the $^4G_{7/2}$ emission lifetime.

Another theory of nonradiative decay derives the multi-phonon rate on basis of energy-transfer theory, as originally described by Forster [6] and Dexter [7]. With the assumption that dipole-dipole interactions dominate the process, and that the phonon absorption $\alpha_{ph}(\lambda)$ is a slowly varying function compared to the emission cross section spectrum $\sigma_{em}(\lambda)$, we derive that.

$$W_{nr} = \frac{2c/3}{(\pi n)^2} \frac{\int \sigma_{em} d\lambda}{V_{min}} \alpha_{ph}, \qquad (2)$$

where $V_{min}$ is the minimum volume that is non-absorbing in nature (centered on the rare earth ion), n is the refractive index, and c is the speed of light. This expression essentially emerges from the well-known Forster-Dexter spectral overlap integral between the emitting and absorbing species, and a volume integration over a uniform acceptor (phonon) concentration, (a derivation similar to other reports in the literature [8-11]). It is also noteworthy however, that the multi-phonon absorption spectrum is commonly described with an exponential expression expression [12,13].

$$\alpha_{ph} = A_{host} \exp\left(\frac{-\gamma_{host} \, h\upsilon_{ph}}{h\upsilon_{char}}\right), \qquad (3)$$

where $\upsilon_{ph}$ is the phonon frequency, $\upsilon_{char}$ is a characteristic phonon frequency of the host material, and $\gamma_{host}$ and $A_{host}$ are other host-dependent constants. So if we combine eqns. (3) and (4), we can suggest an alternative route to deriving the form of the energy gap law·

$$W_{nr}(\upsilon_{gap}) = \frac{2c/3}{(\pi n)^2} \frac{\int \sigma_{em} d\lambda}{V_{min}} A_{host} \exp\left[-\gamma_{host}\left(\frac{h\upsilon_{gap}}{h\upsilon_{max}}\right)\right], \qquad (4)$$

where we have identified $\upsilon_{ph}$ as $\upsilon_{gap}$ and $\upsilon_{char}$ as $\upsilon_{max}$ (maximum phonon frequency), the . The $\gamma_{host}$ parameter turns-out to be similar for many crystals, for instance being in the range of 4-5 for alkali and alkaline-earth halide crystals [13]. The main point to note regarding eqn (4) is that the exponentiated factor in square brackets only contains information concerning the host medium, while the rare earth properties are exclusively represented in the pre-exponential factor – implying that we may expect reasonably good adherence to the form of the energy-gap law, eqn. (1),

We can explore the validity of eqn. (4) by inputting reasonable estimates for the terms in the pre-exponential factor and deducing the magnitude of this constant. Using $V_{min} = 5 \times 10^{-24}$ cm$^3$, $A_{host} = 20,000$ cm$^{-1}$ (average from ref. [13]), and $\sigma_{em}*\Delta\lambda = 1.8 \times 10^{-25}$ cm$^2$ (calculated from Judd-Ofelt theory using the average $\Omega_J$ parameters of YAG and YLF [14]), we obtain a value of $0.6 \times 10^{12}$ sec$^{-1}$, or $\tau_0 = 1.7$ psec, which is defined from eqn. (1) as:

$$1/\tau_o \equiv \frac{2c/3}{(\pi n)^2} \frac{\int \sigma_{em} d\lambda}{V_{min}} A_{host}, \qquad (5)$$

We are now in a position to compare this calculation to the data in Table 1, where we use the energy gap ($\Delta E_{7/2}$) and highest phonon frequencies ($h\upsilon_{max}$) to calculate number of phonons p= $\Delta E_{7/2}/h\upsilon_{max}$. If we also group all of the phosphate glasses into a single datum, and all of the silicates into a second one, then there are potentially ten usable points. Finally, if the LaF$_3$ result is eliminated because of its strongly nonexponential character, the results of the exercise may be displayed as shown in Fig. 3, where we have plotted the nonradiative decay time, $\tau_{7/2}$, against the number of phonons, p. The data is then fitted to the reciprocal of the energy gap law:

$$\tau_{nr} = \tau_0 \exp(a \cdot p) \qquad (6)$$

with the result of the numerical fit yielding $\tau_0 = 3.3$ psec and $a = 3.1$. We are very encouraged by this result because it may be compared with theoretical calculation of $\tau_0 = 1.7$ psec noted above in connection with eqn.

(5). Now, if we associate $\gamma_{host}$ with $a$, and $h\upsilon_{char}$ with $h\upsilon_{max}$, the $a = 3.1$ value from Fig. 3 appears to be within the range of what one may expect from the energy-transfer theory of nonradiative decay encompassed in eqn. (4), since the phonon spectra of many materials is characterized by $\gamma_{host} = 4$-$5$.
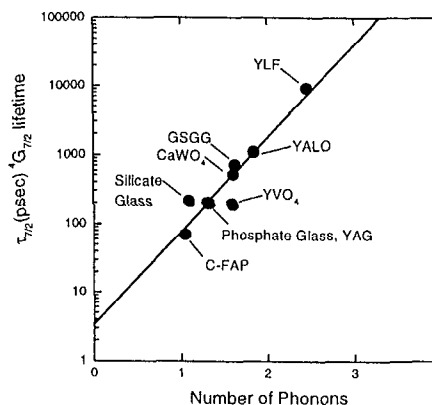


Fig. 3 Plot of the nonradiative decay time against the number of phonons needed to bridge the gap.

In referring back to the more general energy-transfer-based description of nonradiative decay relating to eqn. (2), we can apply another test of this model by plotting $W_m$ of the rare-earth ion against the absorption coefficient $\alpha_{ph}$ of the host and fitting these data to the simple expression:

$$W_{nr} = k\alpha_{ph}, \qquad (7)$$

where k can be theoretically calculated and related to $\tau_0$ by:

$$k = 1/(A_{host}*\tau_0) = \frac{2c/3}{(\pi n)^2} \frac{\int \sigma_{em} d\lambda}{V_{min}} \qquad (8)$$

based on eqns. (2) and (5). In Fig. 4 we have chosen to focus this analysis on data derived exclusively from the YAG, YALO and YLF hosts, because the phonon spectra of these materials have been reported in the literature [15, 16, 17]; in addition, the nonradiative decay rates and the associated energy gaps derived from refs. [18, 19, 20, 21, 22] entail a wide variety of different electronic states and rare earth ions (in contrast to the prior exclusive attention given to the $^4G_{7/2}$ state of Nd$^{3+}$). While we notice that the scatter in the data of Fig. 4 is substantial, it does span many orders of magnitude and the fitted or experimental value of $k_{exp} = 1.0 \times 10^7$ cm/sec based on the data is found to be near

the independently theoretical value of $k = 3 \times 10^7$ cm/sec deduced from eqn. (8) for the $^4G_{7/2}$ state.

Employing the experimental value of k in the simple relationship of eqn. (8): $\tau_0 = 1/(k_{exp}*A_{host})$, we find a third estimate for $\tau_0$ of 5 psec, a value that is in reasonable accord with the theoretically derived value of 1.7 psec from eqn. (5), and the other experimentally determined magnitude of 3.3 psec from Fig. 3 and eqn. (6).
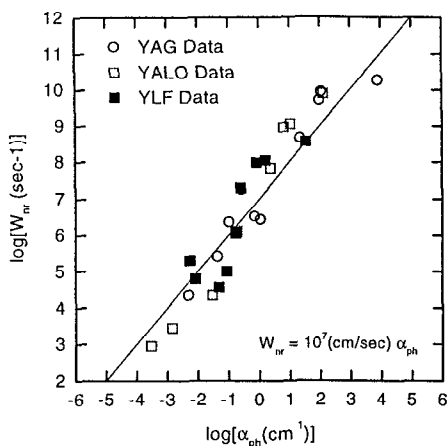


Fig 4. Plot of the nonradiative decay rate of various states of rare earth ions in YAG, YALO, and YLF, as a function of the phonon absorption coefficient of the host at the particular energy gap.

It is important to keep in mind that the results from the first two calculations are specific to the $^4G_{7/2}$ state, while the treatment in the last calculation entails numerous different rare earth ions and states (Fig. 4). The concurrence of these three independent approaches in estimating $\tau_0$ is remarkable and an implicit endorsement of the usefulness of the energy-transfer-based mechanism of nonradiative decay.

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